

Coupled relaxation channels of excitons in monolayer MoSe₂

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Abstract: Using ultrafast degenerate pump–probe spectroscopy, we have investigated the ultrafast exciton dynamics of monolayer MoSe₂ at different pump fluences. The exciton–exciton annihilation, typically occurring tens of picoseconds after pump excitation, has been found to have a substantial correlation with the initial relaxation process dominated by the defect trapping of excitons. A new exciton–exciton annihilation model has been proposed by introducing a coupling term that accounts for the initial relaxation contribution. This coupling term can be tuned by varying the pump excitation intensity and at a high intensity it vanishes due to the full occupation of the defect states. At the same time, the final electron–hole recombination is found to be affected by the heat accumulation effect originating from the high intensity pump pulses.

Coupled relaxation channels of excitons in monolayer MoSe₂[†]

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Using ultrafast degenerate pump-probe spectroscopy, we have investigated the ultrafast exciton dynamics of monolayer MoSe₂ at different pump fluences. The exciton-exciton annihilation, typically taking effect tens of picoseconds after pump excitation, has been found to have a substantial correlation with the initial relaxation process dominated by the defect trapping of excitons. A new exciton-exciton annihilation model has been proposed by introducing a coupling term that accounts for the initial relaxation contribution. This coupling term can be tuned by varying pump excitation intensity and at high intensity it vanishes due to the full occupation of the defect states. At the same time, the final electron-hole recombination is found to be affected by heat accumulation effect originating from the high intensity pump pulses.

1 Introduction

Photo-generated excitons in monolayer transition metal dichalcogenides (TMDCs) are widely investigated in recent years due to their excellent optical properties. Emerging TMDCs materials such as MoS₂, MoSe₂, WS₂ and WSe₂, have sizable bandgaps that change from indirect bandgap to direct bandgap when reduced to monolayer. This electronic bandgap change leads to an extreme enhancement of photoluminescence (PL)¹, which makes these atomically thin materials well suited to a variety of optoelectronic applications, such as LEDs², photodetectors³, and photovoltaics⁴. In addition, due to the high exciton binding energy^{5–8} (on the order of hundreds of meV), these materials have good stability even at room temperature for the application of optoelectronic devices^{9–11}. To apply TMDCs in future optoelectronic devices, it is very important to understand the dynamical behavior of excitons or carriers excited by light. The temporal characteristics of excitons or carriers will determine the performance of the LEDs or photodetectors. Recently, the exciton dynamics in monolayer TMDCs have been investigated via both time-resolved PL and transient pump-probe spectroscopy techniques. According to

the time-resolved PL measurements^{12–14} as well as the theoretical calculations^{15,16}, the average radiative life time of excitons in TMDCs vary from a few picoseconds at low temperature to hundreds of picoseconds or even nanoseconds at room temperature. In addition to the radiative recombination, various exciton scattering mechanisms are revealed through the pump-probe spectroscopy. Exciton-exciton annihilation, an efficient exciton relaxation mechanism occurring within a few tens of *ps*, has been observed in atomically thin MoS₂¹⁷ and MoSe₂¹⁸. Several groups that attribute the initial relaxation process within a few *ps* in single layer MoS₂ to defect states trapping^{19,20}, but Nie et al.²¹ interprets the same span as the carrier cooling. Although different kinds of scattering mechanisms have been proposed, the microscopic mechanisms governing the relaxation process of excitons (or carriers) in TMDCs is still not fully clear. In these previous works, each of the relaxation stages was found to be dominated by a specific relaxation mechanism. It is important to explore if any of these mechanisms are coupled or not, as these mechanisms might take effect in a wide time scale leading to their possible overlaps. Addressing such an aspect will be critical in understanding the relatively complex photo-physics and manipulating the exciton lifetime in TMDCs.

In this article, by employing degenerate pump-probe spectroscopy, we find clear evidence of the correlation between two exciton relaxation channels, where the initial fast decay component facilitates the subsequent exciton-exciton annihilation process in monolayer MoSe₂. A coupling term is introduced to account for the influence of the initial defect trapping process on the following exciton-exciton annihilation. The contribution of this coupling term is found to decrease with the increase of the pump

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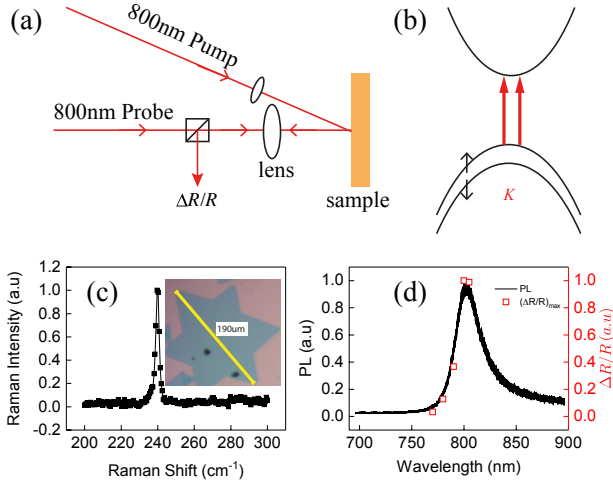


Fig. 1 (a) Diagram of experimental geometry and optical characteristic. Both wavelength of the pump and the probe are 800 nm and the incident angle of the pump beam is around 40° . The probe beam is normally incident. (b) Schematic diagram of the conduction and valence bands at K valley of monolayer MoSe₂. The red arrows represent degenerate pump-probe excitation at A-exciton energy. (c) Raman spectroscopy and the inset is the optical microscope image of monolayer MoSe₂. The sample size is about $190\mu\text{m}$ illustrated by the scale bar. (d) Photoluminescence (PL) spectra and peak differential reflectivity signals as a function of pump-probe energy (red squares) of monolayer MoSe₂

fluence until the saturation of the defect states at high fluences. The final stage of relaxation, which lasts hundreds of picoseconds, is attributed to electron hole recombination as no dependence of the relaxation time on pump injected exciton density is found at low pump fluence.

2 Experimental Section

We performed the degenerate pump-probe spectroscopy of which the experimental configuration is shown in Fig.1 (a), with the pump and probe wavelengths being the same. To avoid the pump beam scattering into the detectors, the probe beam is at normal incidence while the pump beam is around 40 degrees away from the normal direction of the sample plane. This configuration allows us to spatially separate the reflected pump and probe beams. The probe beam is focused on the sample by an aspheric lens with the spot size of about $20\mu\text{m}$ in diameter. Whereas the pump beam is focused by another lens and its spot size is about $38\mu\text{m}$. Fig.1 (b) shows the diagram of the conduction and valence band of monolayer MoSe₂ at K valley. The red arrows represent the degenerate pump-probe excitation at A-exciton resonance. The MoSe₂ samples are grown by chemical vapor deposition (CVD) method with the size larger than $100 \times 100\mu\text{m}$ and all the measurements are performed at room temperature. In this measurement, the polarization of pump and probe beams is orthogonal to each other to further avoid the scattering of pump beams. Under excitation of a 532 nm laser, strong photoluminescence with a central wavelength of 800 nm, a fingerprint of the monolayer MoSe₂, is observed, as shown in Fig.1 (d) (black solid line). Fig.1 (c) presents the Raman spectrum of monolayer MoSe₂ and the

peak at the wave vector of 239.72 cm^{-1} corresponds to the out-of-plane A_{1g} phonon mode. The similar Raman spectra behavior of

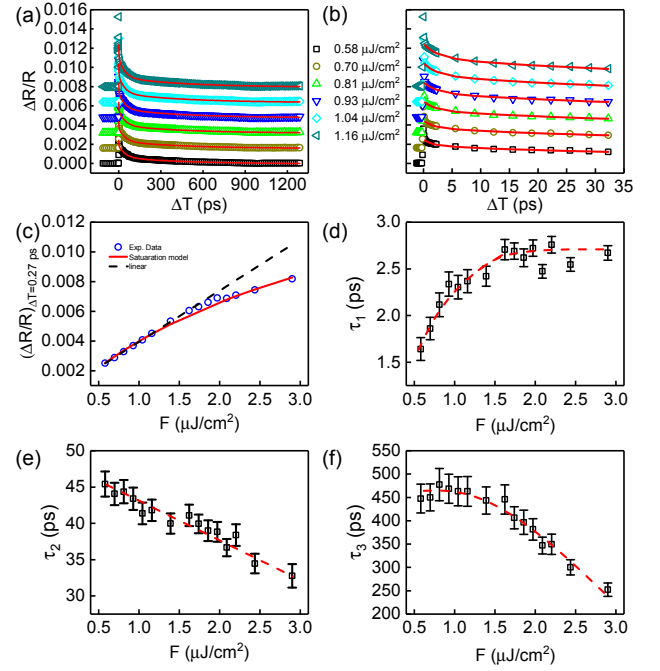


Fig. 2 (a) Transient reflectivity traces under 800 nm degenerate pump-probe measurement at different excitation intensities from $0.58\mu\text{J}/\text{cm}^2$ to $1.16\mu\text{J}/\text{cm}^2$. (b) The zoom in of the first 30 ps of the data shown in (a). (c) Transient reflectivity amplitude at $\Delta T = 0.27\text{ ps}$ under different pump excitations. The saturation trend above $2.20\mu\text{J}/\text{cm}^2$ is obvious. The relaxation time τ_1 , τ_2 , and τ_3 as a function of excitation intensity are shown in (d), (e) and (f), respectively. The red solid lines in (a), (b) and (c) are fitting lines and the red dash lines in (d), (e) and (f) are eye guiding lines.

monolayer MoSe₂ is also reported in many other works^{22–24}. The in-plane mode E_{2g} is not obvious, which may be due to the defect impact. The optical image in the inset of Fig.1 (c) shows a typical monolayer MoSe₂ flake used in our measurement.

3 Results and discussion

Fig.2 (a) shows the transient reflectivity of monolayer MoSe₂ measured at different values of the pump fluence. We perform these measurements under the wavelength of 800nm. For clarity, we only present the data below the pump fluence of $1.16\mu\text{J}/\text{cm}^2$. Here, it is worthy to point out that the pump-probe signals shown in Fig.2 (a) arise from pump injected excitons rather than the line-broadening and peak-shifts which also may be the origin of the pump-induced signals^{25,26}. This is confirmed by the consistency of PL profile and the peak amplitudes of transient reflectivity at different probe energies (Fig.1 (d)). Such assignment can also be found in other works^{17,18}. These dynamic curves are well described by tri-exponential decay function, indicating three distinct exciton relaxation channels characterized by τ_1 , τ_2 and τ_3 are discovered. Note that one should be aware of that each different time constant does not necessarily mean a different relaxation pathway. As reported by Cooney et al^{27,28}, in QD system, 2-3 different channels contribute to the rate process of electron or hole

cooling. Here, our result reveals one more relaxation stage than that reported by Kumar et al.^{18,23} who only observed two relaxation channels in monolayer MoSe₂. A possible reason for this distinction may be that the intra-valley relaxation can be minimized through our degenerate pump probe configuration and thus more refined relaxation dynamics can be observed. More specifically, in the case of non-degenerate pump probe configuration, the pump-generated excitons are not observed until their transition energy can be accessed by the probe wavelength. In addition to the detailed relaxation processes, the resonant A-exciton transition also allows a very fast exciton generation via photo-emission process^{2,18,29} as shown in Fig.2 (b) where the rise-up time is as short as 0.27 ps or less.

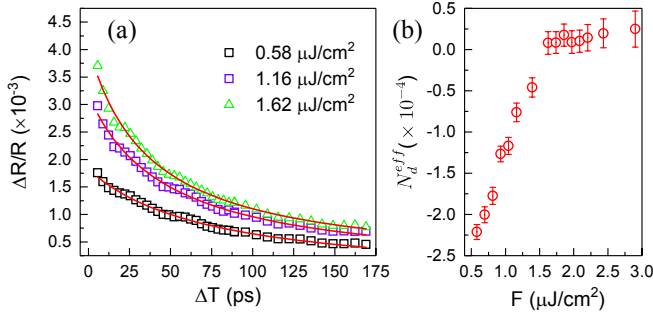


Fig. 3 (a) Transient reflectivity traces at different pump fluences between $\Delta T = 59$ ps and 169 ps. The fitting lines are obtained by the modified exciton-exciton annihilation model (Eq.2). (b) The coupling term N_d^{eff} increases within the fluence range between $0.58 \mu\text{J}/\text{cm}^2$ and $2.9 \mu\text{J}/\text{cm}^2$. The values above the $1.62 \mu\text{J}/\text{cm}^2$ approximately equal to zero.

Figure 2 (c) shows the transient reflectivity amplitude at $\Delta T = 0.27$ ps under different pump excitation intensity. The values of $\Delta R/R$ at $\Delta T = 0.27$ ps increase by a factor of four in the measured pump fluence range, saturating at the highest fluence, which is likely due to the state filling effect near the band edge³⁰. To quantify the pump injected excitons, we employ a saturable absorption model³¹ to fit to these peak values and obtain the saturation pump fluence density of $3.5 \mu\text{J}/\text{cm}^2$. The red solid line in Fig.2 (c) represents the fitting line. Using the absorption coefficient of MoSe₂ reported in previous work³² and the measured pump fluence, we estimate the saturant excitation exciton density to be $1.96 \times 10^{11}/\text{cm}^2$ which is comparable to the reported values of monolayer MoSe₂ in other works^{23,33}. The nonlinear behavior of the peak values of $\Delta R/R$ above $1.74 \mu\text{J}/\text{cm}^2$ also suggests that the photon generated exciton density is close to the highest capacity density. To obtain accurate photon generated exciton density, we calibrated the conversion process of pump power to the pump fluence by measuring the beam spot size carefully (see supporting information). This process helps to optimize the quantitative analysis discussed later. The τ_1 shown in Fig.2 (d) is found to be increased by two times. The similar fluence dependent relaxation component of free carrier is also reported by Nie et. al²¹ in few-layer MoS₂, which is assigned to the hot phonon effect. But in the case of excitons rather than the free carriers, as reported by Robert et al³⁴, the thermalization time is about a few tens of ps. Thus, we could exclude the hot phonon effect

here. The contribution of intrinsic radiative exciton lifetime to this short time scale should be ruled out as in low fluence range it is expected to be independent of excitation fluence³⁵. A possible mechanism accounting for the prolonged fast exciton decay part under high pump fluence is the surface defects scattering. Since at low pump fluences photo-excited carriers can quickly relax into the defect states, while with the pump fluence being high, these defect states are filled gradually, leading to the increase of and its stabilization eventually. As can be seen in Fig.2 (d), the τ_1 remains constant above $1.62 \mu\text{J}/\text{cm}^2$. We also notice that some other group³⁰ reported similar pump fluence dependence of exciton relaxation within the timescale of a few ps, claiming that the defect trapping process dominate this behavior. To visualize this exciton relaxation mechanism, we draw the cartoon picture of this process shown in Fig.4 (a) where the defect density is introduced. After initial fast relaxation into the surface defect states, the populations of excitons are further decreased via exciton-exciton annihilation (EEA) as shown in Fig.2 (e) where the relaxation time decreases with increasing the pump fluences. To verify this assignment, we fit a subrange of the transient traces to an exciton-exciton annihilation model that is expressed as the following:¹⁷

$$N(t) = \frac{N_0}{1 + \gamma N_0 t} \quad (1)$$

where N_0 is the initial photo-generated exciton density and γ is the exciton-exciton annihilation rate. We carefully select the time zone between $\Delta T = 5.6$ ps and $\Delta T = 169$ ps as the relaxation process of τ_2 and fit the data to Eq. 1. According to the fitting results obtained under various pump fluences, we found that the fitted parameter γ above $1.62 \mu\text{J}/\text{cm}^2$ remained almost unchanged indicating that the exciton-exciton annihilation dominated the exciton relaxation at this high pump fluence range. However, for excitation fluences below $1.62 \mu\text{J}/\text{cm}^2$, the fitted γ values increase with the decrease of excitation intensity (see in Fig.S2), which suggests that higher annihilation rate would be required to reduce the population of excitons in the low pump fluence regime. While as reported before by other groups^{17,18}, the annihilation rate between excitons in specific material is constant. Thus, we infer that, in addition to the exciton-exciton annihilation mechanism, one more factor should contribute to the τ_2 decay channel in the low pump excitation range. Meanwhile, it's clearly observed that the pump excitation threshold ($1.62 \mu\text{J}/\text{cm}^2$) below which the γ begins to increase is the same as that where τ_1 begins to decrease (as shown in Fig.2 (d)). Inspired by the similar dependence of τ_1 and γ on pump fluence, we correlate the defect trapping process of τ_1 with the τ_2 relaxation channel. A generalized rate equation describing the exciton dynamics, where both EEA process and radiative exciton lifetimes are considered, has been reported^{17,36}. In addition, Yu et al³⁷ also employed the basic EEA differential equation with additional incident power density term to describe the effect of EEA on luminescence in monolayer TMDs. To better understand the pump fluence dependent coupling strength between the defect trapping and EEA process, we introduce con-

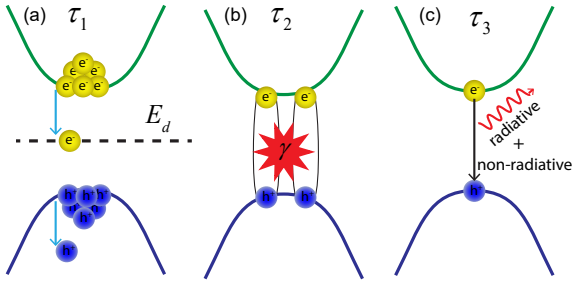


Fig. 4 (a) Excitons are trapped by the defect states. E_d here means the defect energy states. (b) Mutual interactions between excitons that are referred to as the exciton-exciton annihilation and γ is the annihilation rate. (c) Both the radiative and non-radiative electron hole recombination contribute to τ_3 relaxation stage. The wavy line denotes photon emission during the radiative process.

straints into the standard EEA rate equation, written as:

$$\frac{dN}{dt} = -\gamma(N - N_d^{eff})^2 \quad (2)$$

$$N(0) = N_0 + N_d^{eff}; N(\infty) = N_d^{eff}$$

Here, N_0 denotes the initial optical injected exciton population and N_d^{eff} denotes the amount of the excitons trapped by defects at the beginning of EEA (note that N_d^{eff} is a negative value). Since the trapped excitons do not contribute to exciton-exciton annihilation process, the term N_d^{eff} should be subtracted from total exciton density N as expressed in Eq. (2) above. The value of N_d^{eff} is fluence dependent rather than time dependent. The solution of the above equation is

$$N(t) = \frac{N_0}{1 + \gamma N_0 t} + N_d^{eff} \quad (3)$$

We also noticed that several other papers³⁸ have reported coupled dynamics between the trap saturation and EEA. Compared to the coupled differential equations proposed in these works, the modified EEA model in our work (Eq. 3) is very easy to handle, although the former is a more generalized one. The analysis method applied previously in semiconductor quantum dots is also instructive to unravel the details of relaxation pathways and the difference between the relaxation processes^{39,40}.

As shown by the red solid fitting line in Fig.3 (a), we fitted the experimental data very well at low pump fluences using Eq. 3 and obtained a shared global fitting parameter γ which is independent of the excitation intensity as τ_2 expected above. The fitted result of γ is $0.4 \pm 0.01 \text{ cm}^2/\text{s}$, which is not only consistent with the value reported by Kumar et al.¹⁸ but also the same as that above $1.62 \text{ cm}^2/\text{s}$ obtained by Eq. 1, as shown in Fig.S2. The fitting result of N_d^{eff} also supports our assignment. In Fig.3 (b), the amplitude N_d^{eff} decreases as the pump fluence rises close to $1.62 \text{ } \mu\text{J}/\text{cm}^2$ and approximately equals to zero above $1.62 \text{ } \mu\text{J}/\text{cm}^2$. The negative sign means the absorbed excitons by defects. As reported by Wang et al⁴¹, under high exciton density, the exciton-exciton interaction is preferable or more efficient than other mechanisms such as electron-hole recombination and defect scattering. As a result, with the increase of the photo gen-

erated exciton density, the contribution of exciton-exciton annihilation becomes dominant making the defect trapping contribution gradually decreases. More specifically, as the exciton density increases, the effective defect states are gradually fulfilled resulting in the decrease of the amplitude of N_d^{eff} . This finding also suggests that if one wants to avoid the impact of defects on exciton-exciton annihilation, a proper selection of pump fluence would work. Similar experimental results have been reported previously in QD system. Tyagi et al^{42,43} have found that, due to surface trapping, high pump fluence can affect exciton dynamics and the exciton annihilation can be controlled via surface treatment. These results also uncovered the correlation between defect trapping and EEA.

After being trapped by the defect states that followed by the bi-exciton interaction relaxation, the excitons of monolayer MoSe₂ finally relax to an equilibrium state within a long-time scale of a few hundreds of picoseconds, which is usually assigned to both the electron-hole recombination process^{18,44}. At the same time, after τ_1 and τ_2 relaxation processes, the remained exciton population are far below the threshold where exciton-exciton interaction begins to be dominated. Therefore, many body interaction of excitons can be ignored and we contribute the τ_3 relaxation regime to an isolated exciton recombination process. As shown in Fig.4 (c), both the radiative and non-radiative recombination processes may contribute to the exciton recombination. The wavy line denotes photon emission during the radiative electron-hole recombination. The time scale of the electron-hole recombination in our measurement is consistent with that reported by other groups^{12,45}.

However, as shown in Fig.2 (f), the τ_3 values are influenced by pump fluence at relatively high intensity range, which contradicts the independence of electron hole recombination lifetime with pump excitation intensity as reported by Cui et al³⁵. Considering this, we infer that the τ_3 values are also affected by other factors in high fluence range. Back to the original experimental data as shown in Fig.S3, it is clearly observed that the transient $\Delta R/R$ traces are almost overlapped between $\Delta T = 200$ and 400 ps . This period can be safely assigned to the time window of the τ_3 relaxation process as the τ_1 and τ_2 relaxation processes correspond to the time zone before $\Delta T = 175 \text{ ps}$ as shown in Fig. 3 (a). Since the transient $\Delta R/R$ traces are overlapped at the beginning of τ_3 relaxation process, the τ_3 relaxation time should be constant for all the fluences as expected. Whereas after around $\Delta T = 400 \text{ ps}$, the traces that correspond to the fluences above $1.62 \text{ } \mu\text{J}/\text{cm}^2$ begin to separate. The up-going trend after $\Delta T = 400 \text{ ps}$ under high pump fluences indicates an additional factor makes it difficult for the excitons to relax. Generally, the heat diffusion is possible in such a time scale. We also note that the high repetition rate of pulse laser system would have the possibility to lead to a significant heat accumulation effect if the thermal dissipation in the sample is not efficient enough as discussed by Shi et al²⁰. Thus, a possible explanation accounting for the behavior of τ_3 under high pump fluence is the effect of accumulated heat from the pulse laser. Our results indicate that any possible different diffusion rates for different substrates may have different impacts on the behavior of τ_3 .

4 Conclusions

In conclusion, we have studied three distinct relaxation channels in monolayer MoSe_2 by varying the pump intensity using the degenerate ultrafast pump-probe spectroscopy. Our results reveal for the first time the correlation between the different exciton relaxation channels in MoSe_2 . The exciton-exciton annihilation process is found to be mediated by the defect trapping process that accounts for the initial fast excitons decay at low pump fluence. We have employed an improved exciton-exciton annihilation model with the introduction of a pump-fluence dependent coupling term and it agrees well with the experimental observations. The final electron-hole recombination is demonstrated to be independent on pump-injected excitons, although it is affected by the heat accumulation under high excitation intensity. Our findings provide new insights into the exciton relaxation dynamics in terms of the coupled relationship between different decay channels, and at the same time, demonstrate that the pump fluence can be utilized to tune the specific relaxation process, which is important to potential optoelectronic applications of the TMDC materials.

Author contributions

X.Z.R., F.W., and Y.B.X. conceived the project and Y.B.X. supervised the project. Y.Z.M. and F.Q.S. prepared the monolayer MoSe_2 samples by CVD method. B.L. performed ultrafast pump-probe experiments. B.L., X.Z.R., F.W., F.Q.S., W.Q.L., X.F.W., J.W., L.H., R.Z. and Y.B.X. contributed to the analysis of the experiment data. B.L. wrote the paper with all authors contributing to discussion and preparation of the manuscript.

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References

- 1 A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli and F. Wang, *Nano Letters*, 2010, **10**, 1271–1275.
- 2 P. Tonndorf, R. Schmidt, P. Böttger, X. Zhang, J. Börner, A. Liebig, M. Albrecht, C. Kloc, O. Gordan, D. R. T. Zahn, S. Michaelis de Vasconcellos and R. Bratschitsch, *Optics express*, 2013, **21**, 4908–4916.
- 3 Z. Yin, H. Li, H. Li, L. Jiang, Y. Shi, Y. Sun, G. Lu, Q. Zhang, X. Chen and H. Zhang, *Acs Nano*, 2012, **6**, 74–80.
- 4 A. Polman and H. A. Atwater, *Nature Materials*, 2012, **11**, 174–177.
- 5 K. He, N. Kumar, L. Zhao, Z. Wang, K. F. Mak, H. Zhao and J. Shan, *Physical Review Letters*, 2014, **113**, 026803.
- 6 M. M. Ugeda, A. J. Bradley, S.-F. Shi, F. H. da Jornada, Y. Zhang, D. Y. Qiu, W. Ruan, S.-K. Mo, Z. Hussain, Z.-X. Shen, F. Wang, S. G. Louie and M. F. Crommie, *Nature Materials*, 2014, **13**, 1091–1095.
- 7 A. Chernikov, T. C. Berkelbach, H. M. Hill, A. Rigosi, Y. Li, O. B. Aslan, D. R. Reichman, M. S. Hybertsen and T. F. Heinz, *Physical Review Letters*, 2014, **113**, 076802.
- 8 G. Wang, X. Marie, I. Gerber, T. Amand, D. Lagarde, L. Bouet, M. Vidal, A. Balocchi and B. Urbaszek, *Physical Review Letters*, 2015, **114**, 097403.
- 9 F. Withers, O. Del Pozo-Zamudio, S. Schwarz, S. Dufferwiel, P. M. Walker, T. Godde, A. P. Rooney, A. Gholinia, C. R. Woods, P. Blake, S. J. Haigh, K. Watanabe, T. Taniguchi, I. L. Aleiner, A. K. Geim, V. I. Fal'ko, A. I. Tartakovskii and K. S. Novoselov, *Nano Lett.*, 2015, **15**, 8223–8228.
- 10 F. Withers, O. Del Pozo-Zamudio, A. Mishchenko, A. P. Rooney, A. Gholinia, K. Watanabe, T. Taniguchi, S. J. Haigh, A. K. Geim, A. I. Tartakovskii and K. S. Novoselov, *Nature Materials*, 2015, **14**, 301–306.
- 11 A. Pospischil, M. M. Furchi and T. Mueller, *Nat Nanotechnol*, 2014, **9**, 257–261.
- 12 T. Korn, S. Heydrich, M. Hirmer, J. Schmutzler and C. Schuller, *Applied Physics Letters*, 2011, **99**, 102109.
- 13 G. Wang, L. Bouet, D. Lagarde, M. Vidal, A. Balocchi, T. Amand, X. Marie and B. Urbaszek, *Physical Review B*, 2014, **90**, 075413.
- 14 G. Wang, E. Palneau, T. Amand, S. Tongay, X. Marie and B. Urbaszek, *Applied Physics Letters*, 2015, **106**, 112101–5.
- 15 M. Palummo, M. Bernardi and J. C. Grossman, *Nano Lett.*, 2015, **15**, 2794–2800.
- 16 H. Wang, C. Zhang, W. Chan, C. Manolatos, S. Tiwari and F. Rana, *Physical Review B*, 2016, **93**, 045407.
- 17 D. Sun, Y. Rao, G. A. Reider, G. Chen, Y. You, L. Brézin, A. R. Harutyunyan and T. F. Heinz, *Nano Letters*, 2014, **14**, 5625–5629.
- 18 N. Kumar, Q. N. Cui, F. Ceballos, D. W. He, Y. S. Wang and H. Zhao, *Physical Review B*, 2014, **89**, 125427.
- 19 H. Wang, C. Zhang and F. Rana, *Nano Letters*, 2015, **15**, 339–345.
- 20 H. Shi, R. Yan, S. Bertolazzi, J. Brivio, B. Gao, A. Kis, D. Jena, H. G. Xing and L. Huang, *Acs Nano*, 2013, **7**, 1072–1080.
- 21 Z. Nie, R. Long, L. Sun, C.-C. Huang, J. Zhang, Q. Xiong, D. W. Hewak, Z. Shen, O. V. Prezhdo and Z.-H. Loh, *Acs Nano*, 2014, **8**, 10931–10940.
- 22 J. C. Shaw, H. Zhou, Y. Chen, N. O. Weiss, Y. Liu, Y. Huang and X. Duan, *Nano Research*, 2014, **7**, 511–517.
- 23 N. Kumar, Q. Cui, F. Ceballos, D. He, Y. Wang and H. Zhao, *Nanoscale*, 2014, **6**, 4915–4919.
- 24 X. Wang, Y. Gong, G. Shi, W. L. Chow, K. Keyshar, G. Ye, R. Vajtai, J. Lou, Z. Liu, E. Ringe, B. K. Tay and P. M. Ajayan, *Acs Nano*, 2014, **8**, 5125–5131.
- 25 S. Sim, J. Park, J.-G. Song, C. In, Y.-S. Lee, H. Kim and H. Choi, *Physical Review B*, 2013, **88**, 075434.
- 26 C. Ruppert, A. Chernikov, H. M. Hill, A. F. Rigosi and T. F. Heinz, *Nano Lett.*, 2017, **17**, 644–651.
- 27 R. R. Cooney, S. L. Sewall, K. E. H. Anderson, E. A. Dias and

- P. Kambhampati, *Physical Review Letters*, 2007, **98**, 177403.
- 28 R. R. Cooney, S. L. Sewall, E. A. Dias, D. M. Sagar, K. E. H. Anderson and P. Kambhampati, *Physical Review B*, 2007, **75**, 245311.
 - 29 S. Tongay, J. Zhou, C. Ataca, K. Lo, T. S. Matthews, J. Li, J. C. Grossman and J. Wu, *Nano Letters*, 2012, **12**, 5576–5580.
 - 30 M. Seo, H. Yamaguchi, A. D. Mohite, S. Boubanga-Tombet, J.-C. Blancon, S. Najmaei, P. M. Ajayan, J. Lou, A. J. Taylor and R. P. Prasankumar, *Sci Rep*, 2016, **6**, 21601.
 - 31 R. W. Boyd, *Nonlinear Optics*, Academic Press, 2003.
 - 32 A. R. BEAL and H. P. HUGHES, *Journal of Physics C-Solid State Physics*, 1979, **12**, 881–890.
 - 33 N. Kumar, J. He, D. He, Y. Wang and H. Zhao, *Nanoscale*, 2014, **6**, 12690–12695.
 - 34 C. Robert, D. Lagarde, F. Cadiz, G. Wang, B. Lassagne, T. Amand, A. Balocchi, P. Renucci, S. Tongay, B. Urbaszek and X. Marie, *Physical Review B*, 2016, **93**, 205423.
 - 35 Q. Cui, F. Ceballos, N. Kumar and H. Zhao, *Acs Nano*, 2014, **8**, 2970–2976.
 - 36 L. Yuan and L. Huang, *Nanoscale*, 2015, **7**, 7402–7408.
 - 37 Y. Yu, Y. Yu, C. Xu, A. Barrette, K. Gundogdu and L. Cao, *Physical Review B*, 2016, **93**, 201111.
 - 38 T. S. Sosnowski, T. B. Norris, H. H. Wang, P. Grenier, J. F. Whitaker and C. Y. Sung, *Applied Physics Letters*, 1997, **70**, 3245–3247.
 - 39 P. Kambhampati, *Accounts of Chemical Research*, 2011, **44**, 1–13.
 - 40 S. Banerjee, S. Maity and A. Datta, *Journal of Physical Chemistry C*, 2011, **115**, 22804–22809.
 - 41 H. Wang, J. H. Strait, C. Zhang, W. Chan, C. Manolatou, S. Tiwari and F. Rana, *Physical Review B*, 2015, **91**, 165411.
 - 42 P. Tyagi, R. R. Cooney, S. L. Sewall, D. M. Sagar, J. I. Saari and P. Kambhampati, *Nano Lett.*, 2010, **10**, 3062–3067.
 - 43 P. Tyagi and P. Kambhampati, *The Journal of Chemical Physics*, 2011, **134**, 094706–11.
 - 44 Q. Wang, S. Ge, X. Li, J. Qiu, Y. Ji, J. Feng and D. Sun, *Acs Nano*, 2013, **7**, 11087–11093.
 - 45 D. Lagarde, L. Bouet, X. Marie, C. R. Zhu, B. L. Liu, T. Amand, P. H. Tan and B. Urbaszek, *Physical Review Letters*, 2014, **112**, 047401.